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Full communication

## Electrochemical pH sensor based on a hydrogen-storage palladium electrode with Teflon covering to increase stability

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### ABSTRACT

A pH sensor was fabricated using a modified hydrogen-storage palladium electrode. The Pd electrode stores  $H_2$  generated electrochemically at suitable potentials. After the Pd electrode had become coated with palladium hydride ( $PdH_x$ ), the resting potential of the modified Pd electrode responded to changes in the pH with a near-Nernstian response of  $-56.2 \pm 0.2 \text{ mV pH}^{-1}$  in the range from pH 1 to pH 13. Although such Pd electrodes are usually unstable due to the release of  $H_2$ , their stability could be dramatically increased by covering with a Teflon tube. The Pd electrode can be easily regenerated by electrolysis. As  $H_2$  gas is spontaneously released from the modified Pd electrode, the partial pressure of  $H_2$  gas on the surface of the Pd electrode is almost constant ( $H_2$  gas is almost saturated in the vicinity of the electrode). Accordingly, the potential is assumed to be determined by the pH value of the aqueous solution based on the redox potential of the  $H_2/H^+$  couple. When the pH value of the solution is almost constant, the modified Pd electrode can act as a reference electrode without any leakage of the inner electrolyte that occurs with Ag|AgCl|sat. KCl electrodes.

### 1. Introduction

pH is defined as the negative common logarithm of the activity of protons in an aqueous solution. The pH value is one of the most important parameters of a solution and determines the chemical and/or biochemical reactions occurring in this environment. A number of methods for measuring pH have been reported, including color change indicators [1], potentiometry (quinhydrone electrodes [2], glass electrodes [3], hydrogen ( $H_2$ )-generating electrodes [4], metal oxide electrodes [5], liquid-membrane type or film-type proton ( $H^+$ )-selective electrodes [6]), and amperometry [7].

Although pH measurement using acid/base indicators is simple, easy and inexpensive, this method is not suitable for monitoring because it requires periodic sampling or checking with pH-indicator dyes. Similarly, the quinhydrone electrode is not ideal for monitoring applications because it requires the addition of a reagent to the cell system [2]. Hydrogen-generating electrodes using elements such as platinum and palladium (Pd) have also been used as reference or pH-sensing electrodes [8]. However, their application has been limited because of difficulties in the safe handling of  $H_2$  gas. Solid electrodes fabricated from metal oxides and metal hydrides have also been previously reported as pH sensors [9–12]. Metal hydrides such as palladium hydride ( $PdH_x$ ) are particularly attractive because the electrode potentials are

determined by the spontaneous release of  $H_2$  gas from the hydrides. However, they are not widely used because of their instability. In the case of metal oxides, the potential is unstable because the electrode behaviour is determined by multiple reactions. The glass electrode, on the other hand, is the most popular pH-sensing system because of its simplicity, ease of use, and stability [2]. However, it is fragile and difficult to miniaturize. The alkaline error also influences pH detection to some extent. In the case of proton-selective electrodes, the detection range is much smaller than that of other methods ( $H_2$ -generating electrodes, metal oxide electrodes and the glass electrode) [13].

In the present study, a stable pH-responsive electrode based on palladium was developed and the mechanism of the pH response of the electrode was investigated in detail. Palladium electrodes are tough and easy to miniaturize and properties such as the response, selectivity, stability and acid/alkaline error demonstrate their usefulness as a pH sensor. As the Pd electrode does not release harmful substances and can also be renewed by electrolysis to generate  $H_2$  gas, it could be used for on-site monitoring in medical, agricultural, food, and engineering applications. Furthermore, the Pd electrode can be used as a reference electrode if the pH of the test solution is almost constant.

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## 2. Experimental

### 2.1. Reagents

All solutions were prepared using UL-PURE water (Komatsu Electronics Co., Ltd., Japan) with a resistivity of 18.2 MΩ cm at 25 °C. HCl, KCl, NaCl, LiCl, potassium hydrogen phthalate (KHP), di-sodium hydrogen phosphate, sodium bicarbonate and sodium hydroxide were purchased from Wako Co., Ltd. (Japan). A Pd rod (outer diameter: 2 mm, length: 100 mm, 99.9%) was obtained from Nilako Co., Ltd. (Japan). All the chemicals were reagent grade and were used without further purification.

### 2.2. Instruments and fabrication

Potentiometric measurements were conducted using an electrometer HE-106A (Hokuto Denko Co., Ltd., Japan). Cyclic voltammograms were measured using a potentiostat/galvanostat HA1010mM1A (Hokuto Denko Co., Ltd., Japan), a function generator HB305 (Hokuto Denko Co., Ltd., Japan), and an A/D converter GL900, (Graphtec Co., Ltd., Japan).

Electrolysis was carried out using a potentiostat/galvanostat HA1010mM1A (Hokuto Denko Co., Ltd., Japan). One end of the Pd metal rod, which was sealed within a Teflon tubular rod (outer diameter: 10 mm, inner diameter: 2 mm, and length: 20 mm, SANPLATEC Co., Ltd., Japan), was consecutively polished with sandpaper of #80, #240, and #1000 grit, and with abrasive alumina filaments (1 μm in diameter). The rod was then washed for 30 min in an ultrasonic cleaner. The modified Pd electrode was prepared by potential-controlled electrolysis at −0.9 V in a 0.1 M HCl solution. H<sub>2</sub> gas was generated on the surface of the Pd electrode, as shown in Fig. S1. Because the surface of the Pd electrode was covered with H<sub>2</sub> bubbles, the current decreased, as indicated in Fig. S2 and finally became 0 A. This operation was repeated several times until the electrolysis charge reached 2.5 C.

Fabrication of K<sup>+</sup>-ion selective electrodes (ISE) is described in the SI.

### 2.3. Electrochemical measurements

Cyclic voltammograms were obtained using a three-electrode cell system. A Pd electrode, a platinum wire, and an Ag|AgCl|sat. KCl electrode was used as the working, counter and reference electrodes, respectively. Potentiometric measurements for pH sensing were conducted using a two-electrode cell system. The modified Pd electrode and the Ag|AgCl|sat. KCl electrode were utilized as the pH-sensing and reference electrodes, respectively. Potentiometric measurements of K<sup>+</sup> concentration using a K<sup>+</sup> ion-selective electrode (K<sup>+</sup>-ISE) were also carried out with the modified Pd and Ag|AgCl|sat. KCl electrodes as reference electrodes.

### 2.4. Microscopy

SEM images were obtained using a field emission scanning electron microscope (FE-SEM, SU8000, Hitachi High-Technologies, Japan). The accelerating voltage was 1 kV.

## 3. Results and discussion

### 3.1. pH detection

The resting potential of the unmodified Pd electrode was not affected by the pH, and had a value of about +0.1 V. After storage of H<sub>2</sub> through electrolysis, the Pd electrode became responsive to the pH value of the test solution. Fig. 1 illustrates the dynamic response characteristics of the unmodified and modified Pd electrodes in the pH range from 1 to 13. The buffer reagents used here are specified in

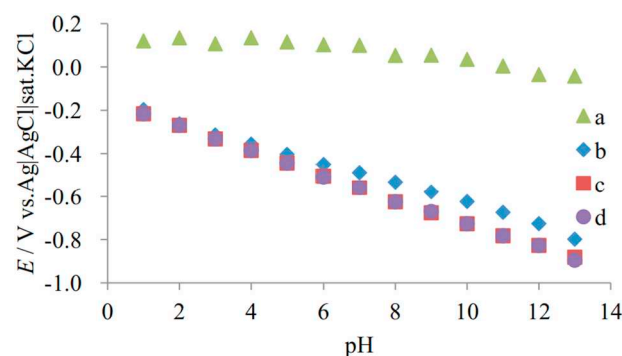


Fig. 1. The relation between the resting potential of the modified palladium electrode and pH. Coulomb number: (a) 0 C, (b) 0.5 C, (c) 2.5 C, and (d) 5.0 C.

Table 1

Test buffer solutions for various pH values.

pH	Buffer solution
1–2	HCl
3–6	KHP
7–8	PBS
9–11	NaHCO <sub>3</sub>
12–13	NaOH

Table 1. In order to store H<sub>2</sub> gas in the Pd electrode, a potential of −0.9 V was applied to the Pd electrode. The Pd electrode with a charge of 0.5C (◆) exhibited a linear response to the concentration of protons with a slope of  $-47.0 \pm 0.2 \text{ mV pH}^{-1}$ . When the electric charge increased to 2.5C (■), the slope increased to  $-56.2 \pm 0.2 \text{ mV pH}^{-1}$ . When the charge was 5C (●), the slope remained approximately the same. Constant potential electrolysis was then conducted by applying 0.5 V to remove H<sub>2</sub> from the Pd electrode. After the decomposition of PdH<sub>x</sub>, the Pd electrode became unresponsive to the protons in the test solution (▲). Thus, the proton response mechanism is dependent on the presence of PdH<sub>x</sub>. A Pd electrode electrolyzed to 5 C is hereafter referred to as a modified Pd electrode. The ideal resting potential of the H<sub>2</sub>-generating electrode ( $\Delta\phi_e(\text{H})$ ) is expressed by

$$\begin{aligned}\Delta\phi_e(\text{H}) &= \Delta\phi_e^\ominus - \frac{RT}{2F} \ln \frac{P(\text{H}_2)/P^\ominus}{a_{\text{H}^+}^2} \\ &= \Delta\phi_e^\ominus - \frac{RT}{2F} \ln \frac{P(\text{H}_2)}{P^\ominus} + \frac{RT}{F} \ln a_{\text{H}^+} \\ &= \Delta\phi' - 0.0591 \text{ pH}\end{aligned}\quad (1)$$

Here,  $\Delta\phi_e^\ominus(\text{H})$  is the standard potential of the redox reaction of the H<sub>2</sub>|H<sup>+</sup> couple, R is the gas constant, T is the temperature, P(H<sub>2</sub>) is the partial pressure of H<sub>2</sub> in the aqueous solution, P<sup>⊖</sup> is the standard pressure, a<sub>H<sup>+</sup></sub> is the activity of protons in the aqueous solution, and Δφ' is a constant value. The modified Pd electrode responded to the pH value from 1 to 13 with a slope of about  $-56.2 \pm 0.2 \text{ mV pH}^{-1}$ . In particular, the slope was  $-58.1 \pm 0.2 \text{ mV pH}^{-1}$  in the pH region from 1 to 9. Considering the activity of H<sup>+</sup> based on the Debye–Hückel limiting law, the slope in the pH region from 1 to 13 was  $-57.2 \pm 0.2 \text{ mV pH}^{-1}$ . The slope in the pH region from 1 to 9 was then  $-60.0 \pm 0.2 \text{ mV pH}^{-1}$ . The slope showed an almost Nernstian response. A practical response experiment was conducted from pH 13 to pH 1. As shown in Fig. S3, the response time was less than 5 s. The potential fluctuations at pH 1, 7, and 13 at 25 °C were within ± 2 mV over a period of 24 h, as shown in Fig. S4. The modified Pd electrode was used in phosphate buffer solution (pH 7) for three weeks, and the potential changed by less than 5 mV. In this case, the Teflon tube covering the modified Pd electrode prevented the release of hydrogen from the modified Pd electrode, as shown in Fig. 2. Although the potential of the modified Pd electrode covered with the Teflon tube was

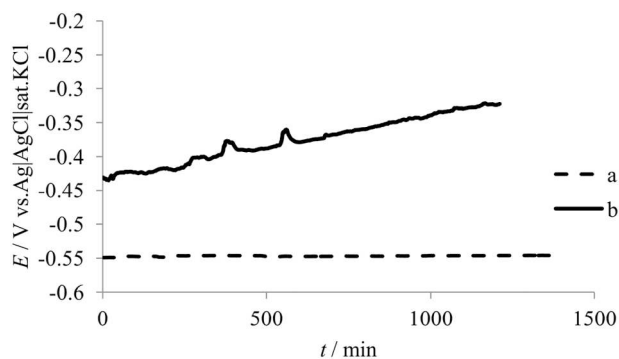


Fig. 2. Changes in the resting potential of the palladium hydrogen storage electrode over time: (a) covered with a Teflon tube (b) without a Teflon tube (at pH 7).

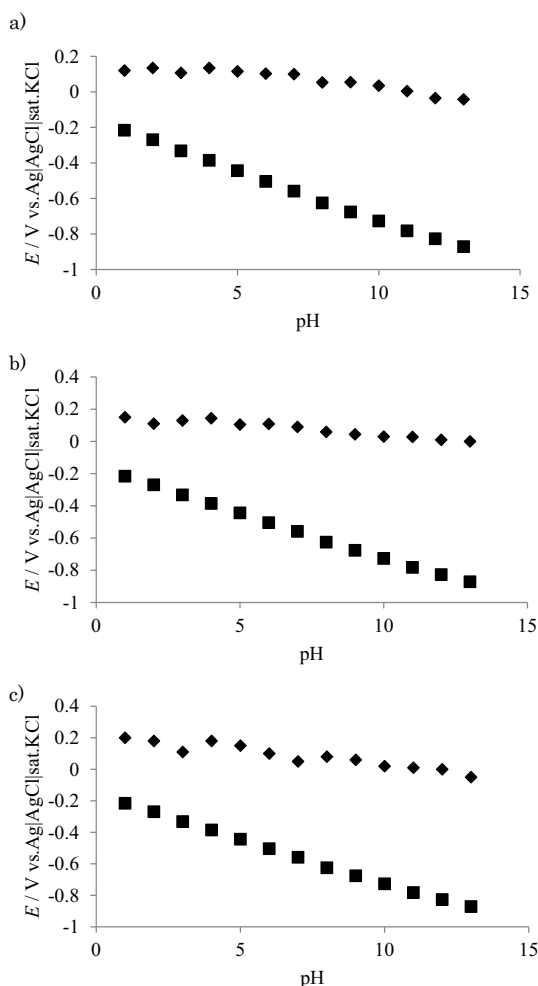


Fig. 3. Potential responses of the modified and unmodified palladium electrode to pH (■: the hydrogen storage electrode, ◆: the metal electrode without hydrogen) for (a) first cycle, (b) second cycle, and (c) third cycle of the repetition of the electrolysis. The hydrogen storage electrode was prepared by electrolysis at  $-0.9$  V to be  $2.5$  C. The metal electrode (without hydrogen) was prepared by electrolysis of the modified palladium electrode at  $0.5$  V to release hydrogen gas.

almost constant, in the absence of the Teflon tube the potential changed almost immediately. Fig. 3 exhibits the potential responses obtained when the modified Pd electrode was repeatedly regenerated. The potential responses of the originally modified Pd electrode and the Pd metal electrode after  $H_2$  was removed are shown in Fig. 3a as the first

cycle. Similarly, the potential responses of second and third cycles are indicated in Fig. 3b and c. Because the modified Pd electrode can be renewed by electrolysis, it is very useful as a pH sensor or reference electrode.

### 3.2. Scanning electron microscopy (SEM) images

Fig. 4 shows the SEM images of the surface of the bare Pd electrode before and after the electrolysis. The surface of the Pd electrode was smooth and homogenous before the electrolysis. After electrolysis with a charge of  $2.5$  C, the SEM image shows that the electrode surface is coated with crystals with a diameter of about  $1\ \mu\text{m}$ . The electrode deposits are assumed to be  $\text{PdH}_x$  on the basis of the discussion above.

### 3.3. Electrochemical reaction

Fig. S5 shows the cyclic voltammograms obtained at pH 1, 7, and 13. A large cathodic peak was observed at about  $-0.8$  V in  $0.1$  M HCl (pH 1). This cathodic peak was caused by the reduction of  $H^+$  to  $H_2$  [14]. In this case, a portion of the  $H_2$  gas generated by the reduction of  $H^+$  was stored in the Pd electrode and  $\text{PdH}_x$  is assumed to be formed (Eq. (2)).



At pH 7 and 13, the cathodic peak currents decreased with a decrease in the concentration of  $H^+$  in the aqueous solution. Since the cathodic peak height was proportional to the concentration of HCl, as shown in Fig. S5, it is evident that the cathodic wave at  $-0.8$  V was caused by the reduction of  $H^+$  to  $H_2$ .

Fig. 5 shows four CV cycles observed in  $0.1$  M HCl using the unmodified Pd electrode. The initial potential was  $-0.2$  V, and the potential was scanned between  $0.8$  V and  $-1.5$  V at a scan rate of  $0.05\ \text{V s}^{-1}$ . No anodic current wave was observed in the first cycle. However, an anodic peak appeared at  $0.5$  V after the second cycle. As the redox potential of the  $H_2/H^+$  couple in  $1$  M HCl (pH 0) is  $-0.2222$  V, it seems that the cathodic peak was caused by both the release of  $H_2$  gas from the Pd electrode and the oxidation of  $H_2$  to  $H^+$  [14]. Therefore, the anodic wave was not observed in the first cycle, and only appeared following the formation of  $\text{PdH}_x$  layers after the second cycle. The zero-current potential shifted about  $0.1$  V in the negative direction, as indicated by the inset of Fig. 5. After electrolysis to store  $H_2$  gas in the Pd electrode, the modified Pd electrode was washed and dried. The Pd electrode expanded out of the Teflon insulant. A constant-potential electrolysis was then conducted at  $0.5$  V to release the  $H_2$  gas. During the electrolysis, bubbles of  $H_2$  gas were observed (Fig. S6) and the expanding part of the modified Pd electrode returned to its original state. The cathodic peak around  $0.5$  V is believed to be caused by both the release of  $H_2$  gas from the modified Pd electrode and the oxidation of  $H_2$  to  $H^+$ . In addition, the height of the cathodic peak decreased after the third cycle. Thus, the redox potential of the  $H_2/H^+$  couple was determined to be about  $-0.2$  V at pH 1. The height of the cathodic peak observed around  $-0.9$  V was proportional to the square root of the potential scanning rate and to the concentration of  $H^+$ , as shown in Figs. S7 and S8, which implied that the reaction was controlled by the diffusion of  $H^+$ .

### 3.4. Acidic and alkaline errors

The acidic and alkaline errors of the modified Pd electrode were also investigated. For HCl concentrations ranging from  $1$  M to  $12$  M, the resting potential shifted in the positive direction in comparison with the calculated values, as illustrated in Fig. 6. Darrell et al. reported that when the glass electrode is used as a pH meter the potential change increased with a decrease in the pH value below pH 0 [15]. The modified Pd electrode showed the same trend as the glass electrode, as shown by the inset in Fig. 6.



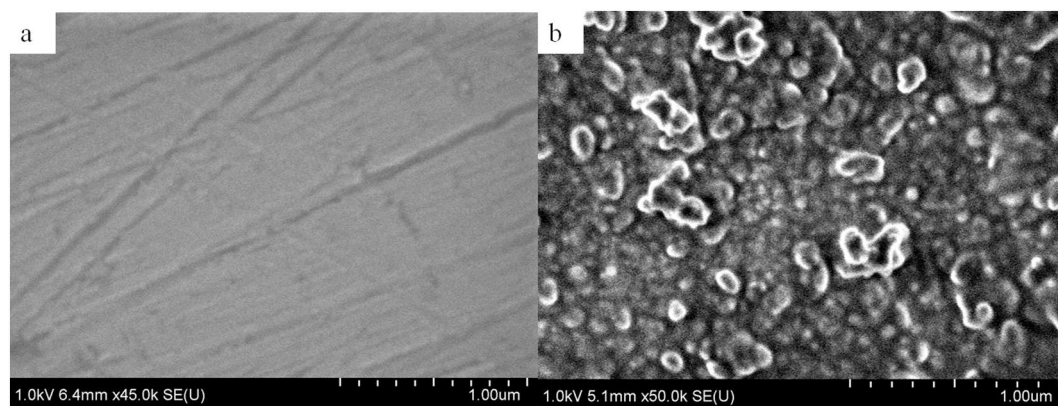


Fig. 4. SEM images of the palladium electrode (a) before and (b) after electrolysis.

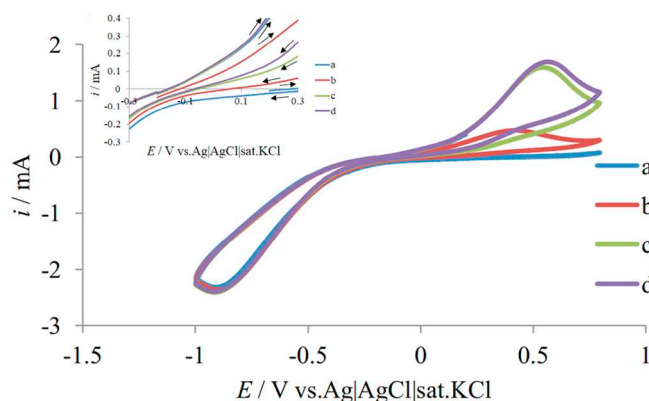


Fig. 5. Cyclic voltammograms of the palladium electrode in 0.1 M HCl at a scanning rate of  $0.05 \text{ V s}^{-1}$ . (a) First cycle; (b) second cycle; (c) third cycle; and (d) fourth cycle. Inset: enlarged graph of the potential region between  $-0.3$  and  $0.1 \text{ V}$ . (a) First cycle; (b) second cycle; (c) third cycle; and (d) fourth cycle.

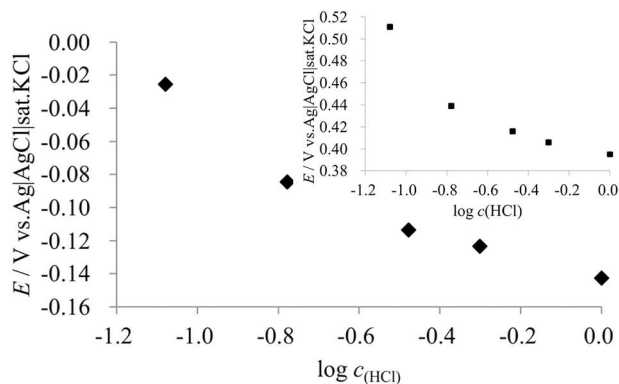


Fig. 6. Acid error for the modified palladium electrode in HCl solution. Inset: Acid error for the glass electrode.

Regarding the alkaline error, the influence of the presence of  $\text{Li}^+$  on the pH value was observed when the concentration of  $\text{Li}^+$  was higher than  $1 \text{ M}$ , as illustrated in Fig. 7. This can be attributed to the formation of a  $\text{Li-Pd}$  alloy ( $\text{PdLi}_7$ ) [16]. The displacement in the case of the modified Pd electrode was less than half that observed in the case of the glass electrode. In contrast, the presence of  $\text{K}^+$  and  $\text{Na}^+$  had no effect on the pH value. In the case of the glass electrode, the alkaline error appeared in the presence of any alkaline metal ions at concentrations higher than  $0.1 \text{ M}$ . When the concentration of  $\text{Na}^+$  or  $\text{K}^+$  is higher than

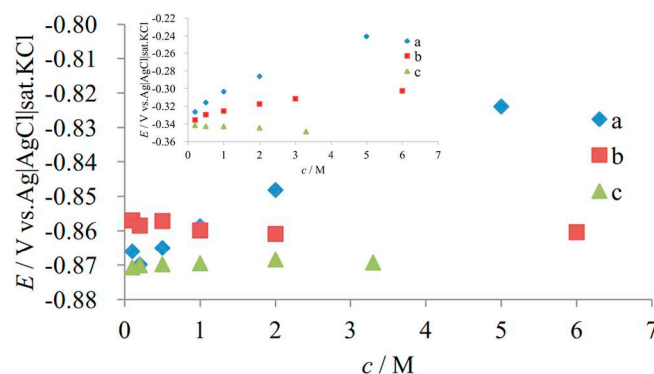


Fig. 7. Alkaline error for the modified palladium electrode in various chloride solutions containing (a)  $\text{Li}^+$ , (b)  $\text{Na}^+$ , and (c)  $\text{K}^+$ . Inset: alkaline error for the glass electrode. (a)  $\text{Li}^+$ ; (b)  $\text{Na}^+$ ; and (c)  $\text{K}^+$ .

$0.1 \text{ M}$  in all systems, the modified Pd electrode is superior to the glass electrode as a pH meter.

### 3.5. Real sample monitoring

Table 2 shows the pH values of various fluids measured using a glass electrode and the modified Pd electrodes. These are in good agreement with each other and reasonably compatible with reported values [17–23]. In addition, calibration curves for the  $\text{K}^+$ -ISE were obtained by using the modified Pd and  $\text{Ag|AgCl|sat. KCl}$  electrodes as reference electrodes. By using the modified Pd electrode as a reference electrode, it is shown that the modified Pd electrode has practical applications, as shown in Fig. S9.

## 4. Conclusions

In the present study, a pH sensor was developed using a modified Pd electrode. The electrode reactions on the surface of the modified Pd electrode were investigated. The modified Pd electrode with  $\text{PdH}_x$  exhibited a good response to the concentration of  $\text{H}^+$ , based on the redox reaction of the  $\text{H}_2|\text{H}^+$  couple. If the pH value of the aqueous solution is almost constant, the modified Pd electrode can be used as a reference electrode without the risk of releasing the inner electrolyte, such as KCl. Since the modified Pd electrode can be regenerated by electrolysis, it is suitable for use as a reference electrode in remote control systems or for environmental observations. The modified Pd electrode is also useful for accurate measurement of the concentration of major nutrition components ( $\text{K}^+$ ,  $\text{Pi}$ , and  $\text{NO}_3^-$ ) in soil because there is no release of electrolytes (KCl, etc.).

**Table 2**  
pH values of various fluids [17–23].

Solution	Glass electrode	Modified Pd electrode	Reported value
Calpis	3.63 ± 0.05	3.96 ± 0.06	3.3 [17]
Milk	6.67 ± 0.03	6.08 ± 0.08	6.4 [18], 7.0 [19]
Vinegar	2.85 ± 0.05	2.49 ± 0.07	2.9 [19]
Soy sauce	3.48 ± 0.04	3.46 ± 0.08	4.8 [20]
Nutrient solution	6.91 ± 0.05	6.65 ± 0.05	6.2 [21]
Coca-Cola	2.79 ± 0.03	2.86 ± 0.03	2.37 ± 0.03 [22], 2.74 ± 0.01 [23]
Coca-Cola Zero	2.86 ± 0.03	2.77 ± 0.06	2.96 ± 0.03 [23]
Drinking yogurt	3.90 ± 0.03	3.34 ± 0.03	4.6 [19], 3.83 ± 0.03 [23]

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2019.03.003>.

## References

- [1] R.W. Sabnis, Handbook of Acid-Base Indicators, CRC Press, San Francisco, 2007.
- [2] J.A. Pierce, H. Montgomery, A microquinhydrone electrode: its application to the determination of the pH of glomerular urine of *Necturus*, J. Biol. Chem. 110 (1935) 763–775.
- [3] P.K. Glasoe, F.A. Long, Use of glass electrodes to measure acidities in deuterium oxide, J. Phys. Chem. 64 (1960) 188–190.
- [4] D.D. Macdonald, P.R. Wentrick, A.C. Scott, Measurement of pH in aqueous systems at elevated temperatures using palladium hydride electrodes, J. Electrochem. Soc. 127 (1980) 1745–1751.
- [5] J. Park, J. Kim, H. Quan, A surface renewable iridium oxide–glass composite hydrogen ion electrode, Microchem. J. 95 (2010) 102–106.
- [6] U. Oesch, D. Ammann, W. Simon, Ion-selective membrane electrodes for clinical use, Clin. Chem. 32 (1986) 1448–1459.
- [7] M. Stred'anský, A. Pizzariello, S. Stred'anská, S. Miertuš, Amperometric pH-sensing biosensors for urea, penicillin, and oxalacetate, Anal. Chim. Acta 415 (2000) 151–157.
- [8] M. Serrapede, G.L. Pesce, R.J. Ball, G. Denuault, Nanostructured Pd hydride microelectrodes: in situ monitoring of pH variations in a porous medium, Anal. Chem. 86 (2014) 5758–5765.
- [9] L. Qingwen, L. Guoan, S. Youqin, Response of nanosized cobalt oxide electrodes as pH sensors, Anal. Chim. Acta 409 (2000) 137–142.
- [10] G.K. Mani, M. Morohoshi, Y. Yasoda, S. Yokoyama, H. Kimura, K. Tsuchiya, ZnO-based microfluidic pH sensor: a versatile approach for quick recognition of circulating tumor cells in blood, ACS Appl. Mater. Interfaces 9 (2017) 5193–5203.
- [11] T. Lindfors, A. Ivaska, pH sensitivity of polyaniline and its substituted derivatives, J. Electroanal. Chem. 531 (2002) 43–52.
- [12] B. Lakard, D. Magnin, O. Deschaume, G. Vanlancker, K. Glinel, S. Demoustier-Champagne, B. Nysten, P. Bertrand, S. Yunus, A.M. Jonas, Optimization of the structural parameters of new potentiometric pH and urea sensors based on polyaniline and a polysaccharide coupling layer, Sensors Actuators B Chem. 166–167 (2012) 794–801.
- [13] W.R. Heineman, H.J. Wieck, A.M. Yacynych, Polymer film chemically modified electrode as a potentiometric sensor, Anal. Chem. 52 (1980) 345–346.
- [14] I. Toru, W. Kirsty-Jo, D. Guy, Fabrication and characterization of nanostructured Pd hydride pH microelectrodes, Anal. Chem. 78 (2006) 265–271.
- [15] D.K. Nordstrom, C.N. Alpers, C.J. Ptacek, D.W. Blowes, Negative pH and extremely acidic mine waters from Iron Mountain, California, Environ. Sci. Technol. 34 (2000) 254–258.
- [16] L.Y. Beaulieu, K.W. Eberman, R.L. Turner, L.J. Krause, J.R. Dahn, Colossal reversible volume changes in lithium alloys, Electrochem. Solid-State Lett. 4 (2001) A137–A140.
- [17] J. Watabe, N. Ikeda, J. Mizutani, N. Sato, S. Jin, T. Hirai, H. Ariga, Comparison of microbiological and chemical characteristics among types of traditionally fermented milk in Inner Mongolia in China and Calpis sour milk (Sannyuu), Milk Sci. 47 (1998) 1–8.
- [18] L.M. Okigbo, G.H. Richardson, R.J. Brown, C.A. Ernstrom, Interactions of calcium, pH, temperature, and chymosin during milk coagulation, J. Dairy Sci. 68 (1985) 3135–3142.
- [19] E. Medina, C. Romero, M. Brenes, A. De Castro, Antimicrobial activity of olive oil, vinegar, and various beverages against foodborne pathogens, J. Food Prot. 70 (2007) 1194–1199.
- [20] N. Nunomura, M. Sasaki, Y. Asao, T. Yokotsuka, Shoyu (soy sauce) volatile flavor components: Basic fraction, Agric. Biol. Chem. 42 (1978) 2123–2128.
- [21] D.S. Domingues, H.W. Takahashi, C.A.P. Camara, S.I. Nixdorf, Automated system developed to control pH and concentration of nutrient solution evaluated in hydroponic lettuce production, Comput. Electron. Agric. 84 (2012) 53–61.
- [22] A. Reddy, D.F. Noorri, S.S. Momeni, B. Waldo, J.D. Ruby, The pH of beverages in the United States, J. Am. Dent. Assoc. 147 (2016) 255–263.
- [23] S. Wongkhantee, V. Patanapiradej, C. Maneenut, D. Tantbirojn, Effect of acidic food and drinks on surface hardness of enamel, dentine, and tooth-coloured filling materials, J. Dent. 34 (2006) 214–220.